

## Supplementary Materials

### **Phosphate removal by ex-situ generated Fe (hydr)oxides from scrap iron electrocoagulation: the critical role of coprecipitation**

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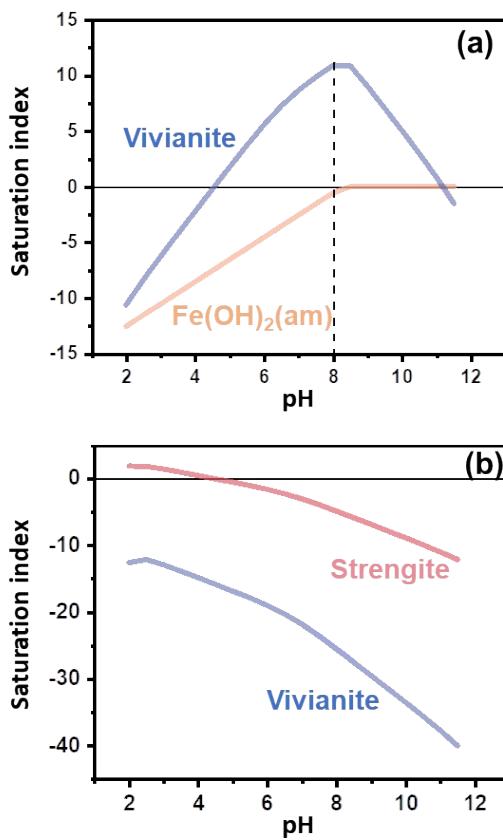
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Supplementary Materials include: Figs. S1–S5, and Tables S1–3.

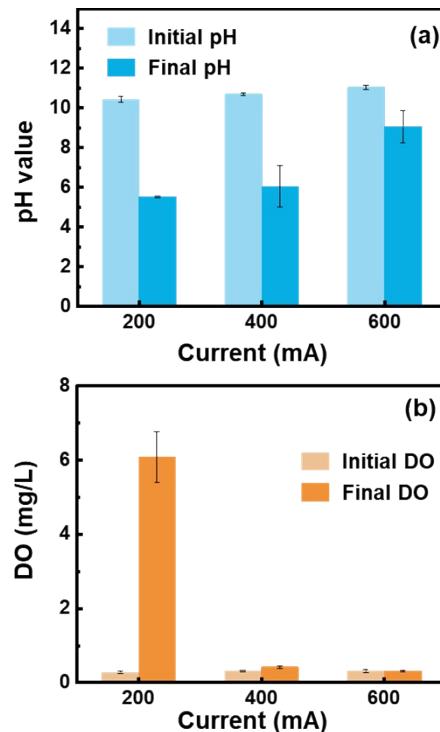


**Fig. S1.** Photo of the electrocoagulation experiment using scrap iron. The cylindrical cell is 128 mm of height and 78 mm of diameter.



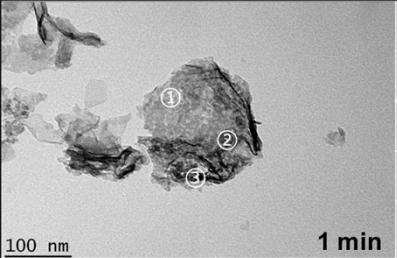
**Fig. S2.** Calculated saturation indexes of (a) vivianite and  $\text{Fe(OH)}_2(\text{am})$  in 0.2 M NaCl, 10 mg/L P as  $\text{PO}_4$ , and 3.1 mM  $\text{Fe(OH)}_2(\text{am})$  (represents the condition of 0 L/min), (b) vivianite and strengite in 0.2 M NaCl, 10 mg/L P as  $\text{PO}_4$ , and 1.0 mM magnetite and

2.1 mM lepidocrocite (represents the condition of 0.25–1.0 L/min) by Visual MINTEQ v3.1. Fe minerals of 3.1 mM were set since which was the amount of Fe dissolved from the anode after 25 min EC, and most of the Fe ions were precipitated before P removal. The thermodynamic parameters used in calculation were presented in Table S1.



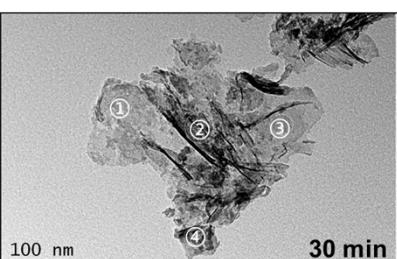
**Fig. S3** Change of (a) pH and (b) DO during the P removal processes by the by the Fe suspension generated from EC under different current intensities. Experiment conditions: [electrolyte]= 0.2 M NaCl, electrolysis for 25 min without aeration,  $[P]_0=10 \text{ mg/L}$ , P reaction time is 300 min.

(a)



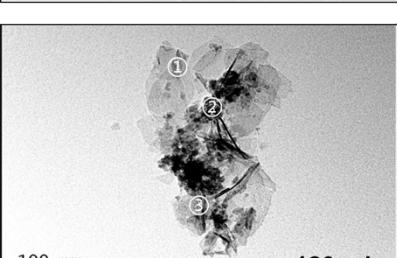
Location	Atomic content of element (%)		
	O(K)	Fe(K)	P(K)
1	64.27	27.19	6.72
2	66.32	24.83	6.36
3	65.21	25.22	6.95

(b)



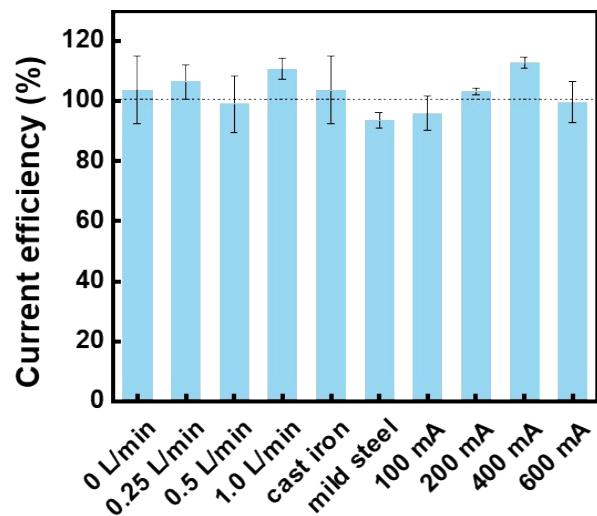
Location	Atomic content of element (%)		
	O(K)	Fe(K)	P(K)
1	69.07	26.97	2.66
2	67.73	29.28	1.53
3	70.67	26.92	2.39
4	67.4	24.27	5.4

(c)



Location	Atomic content of element (%)		
	O(K)	Fe(K)	P(K)
1	69.54	28.6	1.02
2	67.2	30.67	1.3
3	67.06	30.51	1.58

**Fig. S4** Bright field TEM images of the Fe-P solid samples obtained at (a) 1 min, (b) 30 min, and (c) 120 min. The element contents at different locations that identified by EDX were presented in the right.



**Fig. S5** Current efficiency of the EC under variable conditions. Detailed experimental conditions were presented in Table S3.

Table S1 Thermodynamic parameters for species used in calculation in Fig. S2

Species	log K	delta H <sub>r</sub> (kJ/mol)
Fe(OH) <sub>2</sub> (aq)	-20.494	119.62
Fe(OH) <sub>2</sub> <sup>+</sup>	-5.75	37.7
Fe(OH) <sub>3</sub> <sup>-</sup>	-30.991	126.43
Fe(OH) <sub>3</sub> (aq)	-15	75.3
Fe(OH) <sub>4</sub> <sup>-</sup>	-22.7	154.8
Fe <sub>2</sub> (OH) <sub>2</sub> <sup>+4</sup>	-2.894	56.42
Fe <sub>3</sub> (OH) <sub>4</sub> <sup>+5</sup>	-6.288	65.24
FeCl <sup>+</sup>	-0.2	0
FeCl <sup>+2</sup>	1.48	23
FeH <sub>2</sub> PO <sub>4</sub> <sup>+</sup>	22.273	0
FeH <sub>2</sub> PO <sub>4</sub> <sup>+2</sup>	23.85	0
FeHPO <sub>4</sub> (aq)	15.975	0
FeHPO <sub>4</sub> <sup>+</sup>	22.285	-30.5432
FeOH <sup>+</sup>	-9.397	55.81
FeOH <sup>+2</sup>	-2.02	25.1
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	19.573	-18
H <sub>3</sub> PO <sub>4</sub>	21.721	-10.5
HPO <sub>4</sub> <sup>-2</sup>	12.375	-15
Na <sub>2</sub> HPO <sub>4</sub> (aq)	13.32	0
Na <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	2.59	0
NaCl (aq)	-0.3	-8
NaH <sub>2</sub> PO <sub>4</sub> (aq)	19.873	0
NaHPO <sub>4</sub> <sup>-</sup>	13.445	0
NaOH (aq)	-13.897	59.81
NaPO <sub>4</sub> <sup>-2</sup>	1.43	8
OH <sup>-</sup>	-13.997	55.81
Fe(OH) <sub>2</sub> (am)	13.49	-91.62
vivianite	-37.76	5.06
Magnetite	3.4028	-208.5259
Lepidocrocite	1.371	0

Table S2 Fe( $2p_{3/2}$ ) peak fitting data for spectra shown in Fig. 7d–f.

Sample	Binding Energy	FWHM	%Area	Species
1 min	710	1.1	22	Fe(II)-PO <sub>4</sub>
	711	1.1	24	Fe(II)-PO <sub>4</sub>
		sum	46	
	711.6	1.55	27	Fe(III)-OH
	712.7	1.55	20	Fe(III)-OH
	713.8	1.55	7	Fe(III)-OH
	715.1	1.55	0	Fe(III)-OH
		sum	54	
30 min	710	1.1	16	Fe(II)-PO <sub>4</sub>
	711	1.1	24	Fe(II)-PO <sub>4</sub>
		sum	40	
	711.6	1.54	30	Fe(III)-OH
	712.7	1.54	22	Fe(III)-OH
	713.8	1.54	8	Fe(III)-OH
	715.1	1.54	0	Fe(III)-OH
		sum	60	
120 min	710	1.1	16	Fe(II)-PO <sub>4</sub>
	711	1.1	24	Fe(II)-PO <sub>4</sub>
		sum	40	
	711.6	1.56	28	Fe(III)-OH
	712.7	1.56	23	Fe(III)-OH
	713.8	1.56	9	Fe(III)-OH
	715.1	1.56	0	Fe(III)-OH
		sum	60	

Table S3 Experimental conditions of every single pillar in Fig. S5.

Variations	Conditions	Average CE	Error
0 L/min	0.2 M NaCl, cast iron electrode, 200 mA, 10 mg/L PO <sub>4</sub> <sup>3-</sup>	103.6	11.3
0.25 L/min	0.2 M NaCl, cast iron electrode, 200 mA, 10 mg/L PO <sub>4</sub> <sup>3-</sup>	106.4	5.8
0.5 L/min	0.2 M NaCl, cast iron electrode, 200 mA, 10 mg/L PO <sub>4</sub> <sup>3-</sup>	99.0	9.5
1.0 L/min	0.2 M NaCl, cast iron electrode, 200 mA, 10 mg/L PO <sub>4</sub> <sup>3-</sup>	110.7	3.5
cast iron	0.2 M NaCl, 0 L/min, 200 mA, 10 mg/L PO <sub>4</sub> <sup>3-</sup>	103.6	11.3
mild steel	0.2 M NaCl, 0 L/min, 200 mA, 10 mg/L PO <sub>4</sub> <sup>3-</sup>	93.6	2.5
100 mA	0.2 M NaCl, 0 L/min, cast iron electrode, 10 mg/L PO <sub>4</sub> <sup>3-</sup>	96.0	5.8
200 mA	0.2 M NaCl, 0 L/min, cast iron electrode, 10 mg/L PO <sub>4</sub> <sup>3-</sup>	103.1	1.1
400 mA	0.2 M NaCl, 0 L/min, cast iron electrode, 10 mg/L PO <sub>4</sub> <sup>3-</sup>	112.7	1.9
600 mA	0.2 M NaCl, 0 L/min, cast iron electrode, 10 mg/L PO <sub>4</sub> <sup>3-</sup>	99.5	6.9